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(71) Applicant: SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.
Carel van Bylandtlaan 30
NL-2596 HR Den Haag(NL)

(72) Inventor: Post, Martin Franciscus Maria
Badhuisweg 3
NL-1031 CM Amsterdam(NL)
Inventor: van Erp, Willibrord Adelbert
Carel van Bylandtlaan 30
NL-2596 HR The Hague(NL)

(74) Representative: Aalbers, Onno et al
P.O. Box 302
NL-2501 CH The Hague(NL)

(54) Process for the preparation of hydrocarbons.

(57) The invention relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, comprising the steps of:

a) selecting a catalyst comprising:

i) 3-80 parts by weight cobalt per 100 parts by weight of porous carrier;

ii) 0.1-100 parts by weight of at least one metal selected from zirconium, titanium and chromium, per 100 parts by weight of porous carrier; and

iii) an external surface area (S_e)

$S_e \leq 70$ cm^2/ml;

b) activating the catalyst; and

c) contacting the activated catalyst in a fixed bed form with a mixture of carbon monoxide and hydrogen having a hydrogen/carbon monoxide feed ratio (F)

$F \leq 1.9$

under such conditions that

$S_e/F \geq 12.5$, and to hydrocarbons obtained therewith.

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PROCESS FOR THE PREPARATION OF HYDROCARBONS

The invention relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen.

The preparation of hydrocarbons from an H_2/CO mixture by contacting this mixture at elevated temperature and pressure with a suitable catalyst, is known in the literature as the Fischer-Tropsch hydrocarbon synthesis process. The products that can be prepared usually possess a very wide molecular weight distribution and in addition to branched and unbranched paraffins often contain considerable quantities of olefins and oxygen-containing organic compounds. As a rule only a minor portion of the resultant products consists of so-called middle distillates. "Middle distillates" refers to hydrocarbon mixtures having a boiling temperature range principally corresponding to that of the kerosine and gas oil fractions which are obtained in the conventional atmospheric temperature range distillation of crude petroleum. The middle distillate temperature range lies substantially between about 150 and 360 °C. Besides the yield, the pour point of these middle distillates is not optimal. Accordingly, the direct conversion of H_2/CO mixtures by the Fischer-Tropsch process is not a particularly attractive route for the preparation of middle distillates on the technical scale.

Recently a class of Fischer-Tropsch catalysts was discovered which possess the property of providing a product containing only very few olefins and oxygen-containing organic compounds and consisting virtually completely of unbranched paraffins, a substantial proportion of which have a boiling point above the middle distillate range. It has been found that the high-boiling portion of this product can be converted at high yield into middle distillates by means of hydrocracking. The feedstock chosen for the hydrocracking treatment is at least that portion of the product of which the initial boiling point is above the final boiling point of the heaviest middle distillate desired as end product. The hydrocracking treatment, which features a very low hydrogen consumption, yields middle distillates with a considerably better pour point than those obtained in the direct conversion of an H_2/CO mixture by the Fischer-Tropsch process.

The Fischer-Tropsch catalysts belonging to the above-mentioned class contain a porous carrier such as silica, alumina or silica-alumina, and cobalt together with zirconium, titanium and/or chromium as catalytically active metals in such proportions that the catalysts contain 3-80 parts by weight of cobalt and 0.1-100 parts by weight of zirconium, titanium and/or chromium per 100 parts by weight of carrier. The catalysts may be prepared by applying the metals to the carrier by means of kneading and/or impregnation. For further information concerning the preparation of these catalysts by kneading and/or impregnation reference is made to the European patent application 127,220 of Applicant.

In British patent 2,161,177 a similar hydrocarbon synthesis process is disclosed, using Fischer-Tropsch catalysts. The yield of middle distillates, expressed in terms of C_5^+ selectivity, is improved if a catalyst having a specific texture is used, namely an external surface area of 5-70 cm^2/ml, an internal surface area (S_i) of 10-400 m^2/ml, under the provision that $10^6 > S_e^2 x S_i . 2.5 x 10^4$.

It has now been found that the C_5^+ selectivity of these cobalt promoted catalysts may be further improved if similar catalysts having a specific external catalyst surface area (S_e) are contacted in a fixed bed at a specific hydrogen/carbon monoxide feed ratio (F).

The present invention, therefore, relates to a process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, comprising the steps of:

a) selecting a catalyst comprising:

i) 3-80 parts by weight cobalt per 100 parts by weight of porous carrier;

ii) 0.1-100 parts by weight of at least one metal selected from zirconium, titanium and chromium, per 100 parts by weight of porous carrier; and

iii) an external surface area (S_e)

$S_e \leq 70$ cm^2/ml;

b) activating the catalyst; and

c) contacting the activated catalyst in a fixed bed form with a mixture of carbon monoxide and hydrogen having a hydrogen/carbon monoxide feed ratio (F)

$F \leq 1.9$

under such conditions that

$S_e/F \geq 12.5$.

The external catalyst surface area S_e may be determined for a representative sample of a given volume expressed in ml, by determining the external surface area expressed in cm^2 of each of the catalyst particles present therein, by summing the external surface areas found and by dividing the sum by the volume of the sample.

The porous carrier to be used in the process of the present invention is preferably silica, alumina, silica-alumina or titania, especially silica. The average size of the catalyst particles is suitably between 0.2 and 5 mm, preferably between 0.5 and 3 mm more preferably between 1 and 2.5 mm.

The cobalt promoted catalysts used in the process of the invention are preferably prepared by one of the following procedures:

a) cobalt is first applied by impregnation in one or more steps and subsequently the other metal is likewise applied by impregnation in one or more steps;

b) the other metal is first applied by impregnation in one or more steps and subsequently cobalt is likewise applied by impregnation in one or more steps;

c) cobalt is first applied by kneading in one or more steps and subsequently the other metal is applied by impregnation in one or more steps;

d) cobalt and the other metal are applied by kneading in one single step; or

e) the carrier material is extruded followed by impregnation with cobalt and/or the other metal.

In the process according to the invention the cobalt promoted catalysts preferably contain 15-50 parts by weight cobalt per 100 parts by weight carrier. The quantity of other metals, when present, depends among other things on the manner in which these metals are applied. In the above procedure a) the catalysts finally contain 0.1-5 parts by weight of the other metals per 100 parts by weight carrier. In procedure b) the catalysts contain preferably from about 5 to 40 parts by weight of the other metals per 100 parts by weight carrier. It is preferred to use as the other metal zirconium and as carrier silica.

It was rather surprising to find that the C_5^+ selectivity improved at the specific external catalyst surface area (S_e) at feed ratios lower than 1.9, because as the feed ratio decreases, the occurrence of the so-called Boudouard-reaction increases, especially in the downstream part of the reactor, resulting in a conversion of carbon monoxide into carbon dioxide and carbon. The carbon will deposit on the catalyst, which deposition is detrimental to the catalyst activity. The hydrocarbon/carbon monoxide mixture feed used in the process according to the invention should have a hydrogen/carbon monoxide feed ratio less than 1.9 or at the most equal to 1.9. Preferably the feed ratio is less than 1.75, more preferably less than 1.5, still more preferably at a feed ratio of about 1.1-1.2. It is preferred that the hydrogen/carbon monoxide ratio of the gas mixture leaving the reactor is at least 0.4 (integral conditions).

Preferably the external surface area S_e of the cobalt promoted catalyst is less than 50 cm^2/ml. The best results are obtained with a catalyst having an external surface area S_e of about 20-50 cm^2/ml.

The space velocity of the reaction of the present invention is suitably between 50 and 5000 Nl/l/h, preferably between 300 and 1500 Nl/l/h.

Mixtures of carbon monoxide and hydrogen, which are suitable for the process according to the invention might be obtained by subjecting light hydrocarbons, such as methane, to steam reforming or partial oxidation. Specific preference is given to the use of natural gas as feedstock.

The catalytic process according to the invention is normally carried out at a temperature of 125-350 °C, preferably at a reaction temperature of about 180-250 °C, more preferably 200-230 °C. The reaction pressure is normally 5 to 500 bar abs, preferably 15-50 bar abs, more preferably 20-40 bar abs.

Prior to the catalysts in the process according to the invention, the cobalt promoted catalysts have to be activated. This activation can suitably be carried out by contacting the catalysts at a temperature between 150 and 500 °C with hydrogen or a hydrogen containing gas, preferably at a temperature between 200 and 350 °C.

The height of the catalyst bed may vary between 1 and 20 metres, preferably between 5 and 14 metres.

Although in the preparation of middle distillates the product obtained over the cobalt catalyst it is sufficient to use as feedstock for the hydrocracking treatment that portion of the product of which the initial boiling point is above the final boiling point of the heaviest middle distillate desired as end product, for this purpose it is preferred to use the total C_5^+ fraction of the product prepared with the cobalt catalyst, because it has been found that under the influence of catalytic hydrogen treatment a quality improvement takes place in the gasoline, kerosine and gas oil fractions present therein.

The hydrocracking treatment is carried out by contacting the fraction to be treated, at elevated temperature and pressure and in the presence of hydrogen, with a catalyst containing one or more noble metals of Group VIII on a carrier. The hydrocracking catalyst used is preferentially a catalyst containing 0.1-2% by weight and in particular 0.2-1% by weight of one or more noble metals of Group VIII on a carrier. Preference is given to catalysts containing as Group VIII noble metal platinum or palladium, and silica-alumina as carrier. The hydrocracking treatment is preferentially carried out at a temperature of 200-400 °C and in particular of 275-375 °C and a pressure of 5-200 bar and in particular of 10-75 bar.

The process according to the invention will be further illustrated with reference to the following example.

EXAMPLE

Ten $Co/Zr/SiO_2$ catalysts (catalysts 1-10) were prepared by impregnation of spherical silica carriers with solutions of cobalt and zirconium compounds. In each impregnation step a quantity of solution was used of which the volume of the carrier substantially corresponded to the pore volume of the carrier concerned. After each impregnation step the solvent was removed by heating and the material was calcined at 500 °C. After the final calcination the compositions were activated in hydrogen as follows: catalysts 1 and 4 at 250 °C and catalysts 2, 3 and 5-10 at 260 °C. Catalysts 1-10 were prepared as follows.

Catalysts 1 and 4

One-step impregnation of a silica carrier with an aqueous solution of cobalt nitrate, followed by one-step impregnation of the cobalt-loaded carrier with an aqueous solution of zirconium nitrate.

Catalysts 2, 3 and 5-10

Two-step impregnation of a silica carrier with a solution of zirconium tetra-n-propoxide in a mixture of n-propanol, toluene and acetyl acetone, followed by one-step impregnation of the zirconium-loaded carrier with an aqueous solution of cobalt nitrate.

Further particulars of catalysts 1-10 are shown in the table. The catalysts 1-10 were used for the preparation of hydrocarbons from a mixture of carbon monoxide and hydrogen having H_2/CO molar ratios shown in the table.

The reactions with the various catalysts were carried out with a pre-determined mixture of carbon monoxide and hydrogen, at such a temperature that the space time yield (C_1^+ production (g/l/h)) is 100.

It is apparent from the table that the experiments carried out with the catalysts 1-7 and 9 are according to the invention and show a C_5^+ selectivity of more than 80% by weight, whereas the experiments carried out with the catalysts 8 and 10 show a much lower C_5^+ selectivity (72-78% by weight). Decisive for an improved C_5^+ selectivity is the combination of a specific external catalyst surface area S_e and a specific hydrogen/carbon monoxide feed ratio F, the ratio of these values (S_e/F) should be larger or equal to 12.5, preferably larger than 20, most preferred lying within the range 20-40.

CATALYSTS AND EXPERIMENTAL CONDITIONS AND RESULTS											
Catalyst no.	1	24	2B	3	4	5	6	7	8	9	10
Zr load ppw Zr/100 ppw SiO_2	0.9	12	12	12	0.9	12	12	12	12	12	12
Co load mg Co/ml catalyst	83	102	102	96	90	101	105	102	100	96	101
external surface area S_e (cm^2/ml)	24	23	23	24	22	21	40	20	20	16	14
temperature (°C)	217	210	218	220	225	218	210	225	212	230	225
pressure (bar abs)	20	25	25	25	20	20	25	25	25	25	25
space velocity of H_2 + Co ($N1.1^{-1}.h^{-1}$)	600	600	750	600	600	600	750	600	600	600	750
H_2/CO ratio (F)	1.8	1.8	1.5	1.1	1.5	1.5	1.1	1.1	1.8	1.1	1.8
H_2 + CO conversion (%v)	84	85	72	84	83	84	70	83	85	84	68
C_{1+} production ($g.1^{-1}.h^{-1}$)	101	104	108	102	100	102	106	100	103	101	106
C_{5+} selectivity (%w)	81	84	86	90	81	82	90	87	78	81	72
Se/F	13.33	12.78	15.33	21.82	14.67	14.00	36.36	18.18	11.11	14.55	7.78

Claims

1. Process for the preparation of hydrocarbons by catalytic reaction of carbon monoxide with hydrogen, comprising the steps of:

a) selecting a catalyst comprising:

i) 3-80 parts by weight cobalt per 100 parts by weight of porous carrier;

ii) 0.1-100 parts by weight of at least one metal selected from zirconium, titanium and chromium, per 100 parts by weight of porous carrier; and

iii) an external surface area (S_e)

$S_e \leq 70$ cm^2/ml;

b) activating the catalyst; and

c) contacting the activated catalyst in a fixed bed form with a mixture of carbon monoxide and hydrogen having a hydrogen/carbon monoxide feed ratio (F)

$F \leq 1.9$

under such conditions that

$S_e/F \geq 12.5$.

2. Process as claimed in claim 1, wherein the feed ratio F is less than 1.75.

3. Process as claimed in claim 1, wherein the feed ratio F is less than 1.5.

4. Process as claimed in claim 1, wherein the feed ratio F is about 1.1-1.2.

5. Process as claimed in claims 1-4, wherein the external surface area S_e is less than 50 cm^2/ml.

6. Process as claimed in claims 1-4, wherein the external surface area S_e is about 20-50 cm^2/ml.

7. Process as claimed in claims 1-6, wherein S_e/F is larger than 20.

8. Process as claimed in claims 1-6, wherein S_e/F is about 20-40.

9. Process as claimed in claims 1-8, wherein the porous carrier is silica, alumina, silica-alumina or titania.

10. Process as claimed in claims 1-9, wherein the reaction pressure is about 15-50 bar abs.

11. Process as claimed in claims 1-10, wherein the reaction temperature is about 180-250 °C.

12. Process for the preparation of hydrocarbons as claimed in claim 1, substantially as described herein in particular with reference to the example.

13. Hydrocarbons prepared in accordance with a process as described in any of the claims 1-12.